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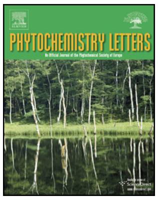

New acylated triterpene saponins from the roots of *Securidaca inappendiculata* Hassk

Haiyan Zha[a], Zhi Wang[a], Xuedong Yang[a,*], Daqing Jin[b], Licui Hu[a], Wenfeng Zheng[a], Lizhen Xu[c], Shilin Yang[d]

[a] School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, PR China
[b] School of Medicine, Nankai University, Tianjin 300072, PR China
[c] Institute of Medicinal Plant Development, Peking Union Medical College and Chinese Academy of Medical Sciences, Beijing 100094, PR China
[d] Jiangxi University of Traditional Chinese Medicine, No. 56 Yangmin Road, Nanchang 330006, PR China

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ABSTRACT

Two new acylated triterpene saponins, named as securioside **C** (**1**), securioside **D** (**2**), and one pair of isomers **3/4**, the (*Z*)–isomer securioside **E** (**3**) being new, together with a known triterpene saponin polygalasaponin XLIV (**4**) were isolated from the roots of *Securidaca inappendiculata* Hassk. Their structures were established by HRESIMS, 1D and 2D NMR experiments and comparison of their NMR data with previous reported data. In addition, Compounds **1–2**,**3/4**, **4** were evaluated for cytotoxicities against LLC (Lewis lung carcinoma) and MCF-7 (human breast cancer) cell lines. Compounds **1** and **2** exhibited moderate cytotoxic activities against LLC cells with IC_{50} values of 45.56 μM and 85.98 μM.

1. Introduction

Securidaca inappendiculata Hassk is a traditional Chinese herbal medicine, belonging to the Polygalaceae family, mainly distributed in Yunnan, Guangxi, Guangdong, and Hainan provinces of southern China and the tropical regions of Asia (Delecti Florae Reipublicae Popularis Sinicae Agendae Academiae Sinicae, 1997). The roots of *S. inappendiculata* are used as an anti-inflammatory, antibacterial, and antirheumatism agent in China (Jiangsu Institute of Botany, 1988). Our previous investigations on this species resulted in the isolation of benzophenones (Yang et al., 2003b) from the chloroform fraction, xanthones (Yang et al., 2001a) from the chloroform/ethyl acetate fractions, xanthone glycosides (Yang et al., 2002a) and organic acids (Yang et al., 2001b) from the ethyl acetate/acetone fractions, and oligosaccharide esters (Yang et al., 2003a) and terpenoic glycosides (Yang et al., 2002b) from the acetone fraction of ethanol extract. Two saponins (Kuroda et al., 2001) obtained from the water extract of the roots of the plant have been reported. Modern pharmacological evaluations revealed that the saponins from the roots of *S. inappendiculata* exhibited macrophage-oriented cytotoxic activity. In our preliminary experiment, the aqueous portion of ethanol extract from the roots of *S. inappendiculata* showed cytotoxic activities in vitro against LLC (Lewis lung carcinoma) and MCF-7 (human breast cancer) cell lines. Therefore, as part of our ongoing investigation of anti-tumor constituents, we reported the isolation and the structural elucidation of two new triterpene saponins, one pair of (*E*)/(*Z*) – isomers (the (*Z*) – isomer being new), and a known triterpene saponin with presenegenin as aglycon (see Fig. 1) isolated from the roots of *S. inappendiculata*. Cytotoxicities of compounds **1–2**, **3/4**, **4** were evaluated against LLC and MCF-7 cell lines, respectively.

2. Results and discussion

Compound **1**, obtained as a white amorphous powder, was assigned a molecular formula of $C_{65}H_{96}O_{28}$ which was deduced from quasi-molecular ion peak ($[M+Na]^+$) at *m*/*z* 1347.6020 in the positive ion mode HRESIMS. The ^1H NMR spectrum of **1** showed signals for five tertiary methyl groups at δ_H 0.76, 0.88, 1.11, 1.48, 1.90, which correlated with five sp^3 C-atoms at δ_C 34.0, 24.3, 19.0, 17.8, 14.6 respectively based on the HSQC spectrum, also an isolated oxymethylene at δ_H 3.78, 4.04 (H_2-27), an oxymethine proton at δ_H 4.68 (H-2), an olefinic proton at δ_H 5.78 (H-12) combined with two sp^2 olefinic carbons at δ_C 128.2 (C-12), 139.2 (C-13), and two carboxylic carbon signals at δ_C 181.0 (C-23), 177.0 (C-28) in the ^{13}C NMR spectrum. These data proved that the aglycone possessed an olean-12-ene-23,28-dioic acid skeleton (Tables 1 and 2), and was in full agreement with those of tenuifolin (3-*O*-β-D-glucopyranosyl presenegenin) in which presenegenin ((2β,3β,4α)-2,3,27-trihydroxyolean-12-ene-23,28-dioic acid)

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* Corresponding author. Tel.: +86 22 87401152.
E-mail address: yangxd@tju.edu.cn (X. Yang).

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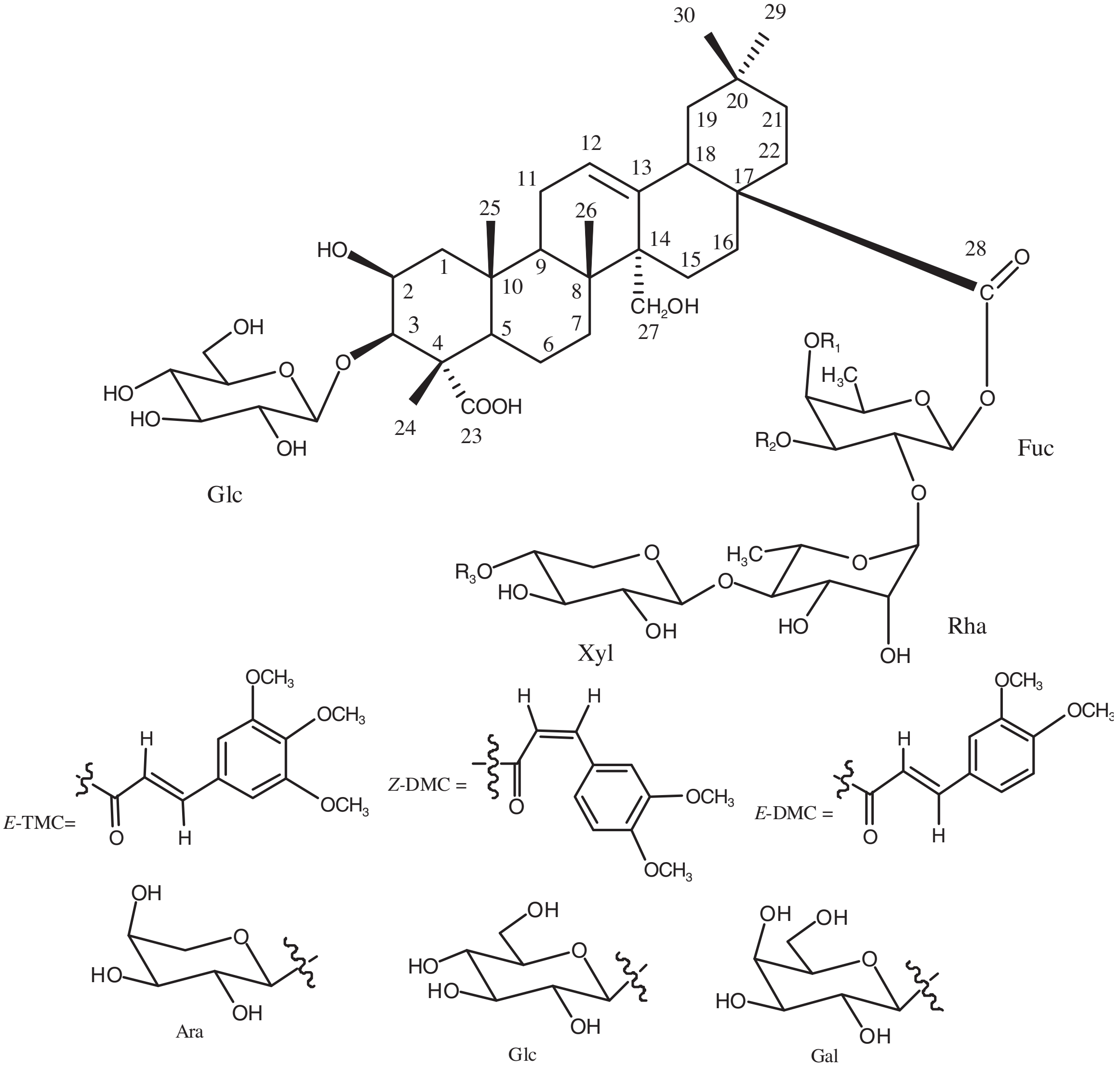

	R1	R2	R3
1	***E*-TMC**	**H**	**H**
2	***E*-DMC**	**Ara**	**H**
3	***Z*-DMC**	**Glc**	**Gal**

Fig. 1. Structures of compounds **1–3**.

was commonly encountered in triterpene saponins isolated from the family Polygalaceae (Mitaine-Offer et al., 2002; Teng et al., 2002; Zhang et al., 1996). The chemical shift values at δ_C 86.3 (C-3) and δ_C 177 (C-28) suggested that the saponin was a bisdesmosidic glycoside with saccharide units attached to these positions. Beside these, the ^{1}H NMR spectrum was also displayed signals of four anomeric protons at δ_H 6.35 (1H, s), 6.17 (1H, d, J = 8.15 Hz), 5.03 (1H, d, J = 5.8 Hz), and 5.02 (1H, s), which gave correlations with four anomeric carbon signals at δ_C 102.0, 94.9, 107.7, and 105.7 in the HSQC spectrum respectively. The COSY, TOCSY, HSQC, and HMBC spectroscopic experiments identified the direct correlations of protons of sugar ring from the readily identifiable anomeric protons (Tables 1 and 2). The coupling constant confirmed the presence of the units of one β-glucopyranosyl, one β-fucopyranosyl, one β-xylopyranosyl, and one α-rhamnopyranosyl. After acid hydrolysis, the sugar units were confirmed to be D-glucose, D-fucose, L-rhamnose, and D-xylose by HPLC analysis of their thiocarbamoyl-thiazolidine derivatives compared with authentic samples.

The HMBC correlation between δ_H 5.02 (1H, s, Glc-1) and δ_C 86.3 (Agly-C-3) and NOE correlation between δ_H 5.02 (Glc-1) and δ_H 4.54 (Agly-H-3) in the NOESY spectrum revealed a linkage between the aglycon and a glucopyranosyl moiety. A correlation in the HMBC spectrum between δ_H 6.17 (1H, d, J = 8.15 Hz) (Fuc-1) and δ_C 177 (Agly-C-28) indicated that a fucose was attached to C-28 of the aglycon. Moreover, in the HMBC spectrum, long-range correlations were observed between the following protons and carbons: δ_H 4.70 (Fuc-2) and δ_C 102.0 (Rha-1), δ_H 4.35 (Rha-4) and δ_C 107.7 (Xyl-1),